

Electron–Phonon Coupling in Charged Buckminsterfullerene

N. Breda^{1,2}, R.A. Broglia^{1,2,3}, G. Colò^{1,2}, H.E. Roman^{1,4}, F. Alasia^{1,2},
G. Onida⁵, V. Ponomarev⁶ and E. Vigezzi²

¹*Dipartimento di Fisica, Università di Milano, Via Celoria 16, I-20133 Milano, Italy.*

²*INFN, Sezione di Milano, Via Celoria 16, I-20133 Milano, Italy.*

³*The Niels Bohr Institute, University of Copenhagen, 2100 Copenhagen, Denmark.*

⁴*Institut für Theoretische Physik III, Universität Giessen, Heinrich-Buff-Ring 16,
35392 Giessen, Germany.*

⁵*Dipartimento di Fisica, Università di Roma Tor Vergata, Via della Ricerca Scientifica 1,
I-00133 Roma, Italy.*

⁶*Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, Dubna,
Head Post Office, P. O. Box 79, Moscow, Russia.*

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Abstract

A simple, yet accurate solution of the electron–phonon coupling problem in C_{60} is presented. The basic idea behind it is to be found in the parametrization of the ground state electronic density of the system calculated making use of ab–initio methods, in term of sp^{2+x} hybridized orbitals. This parametrization allows for an economic determination of the deformation potential associated with the fullerene’s normal modes. The resulting electron–phonon coupling constants are used to calculate Jahn–Teller effects in C_{60}^- , and multiple satellite peaks in the corresponding photoemission reaction. Theory provides an accurate account of the experimental findings.

The discovery of fullerenes [1], and the subsequent “mass synthesis” [2] of these hollow molecules, have prompted the search for a new class of materials such as fullerides (salts like K_3C_{60}), fullerites (C_{60} molecular crystals), etc., in which fullerenes play the role of the building blocks. The understanding of the response of these building blocks to external fields is essential in the characterization of the associated new materials. A central issue in this quest is how the electronic properties of fullerenes are modified by the coupling of electrons to phonons. This question can be answered in terms of ab-initio methods (cf., e.g., Refs. [3,4] and Refs. therein; cf. also Ref. [5]). These methods are, however, computationally demanding and not particularly transparent, and much of the physical insight is lost in the complexity of mathematics.

In the present paper we present a simple, yet accurate solution of the electron-phonon coupling problem particularly suited for fullerenes, and apply it to C_{60}^- . The central idea behind this solution is based on a parametrization of the ground state electronic density of the system calculated making use of ab-initio methods in terms of hybridized atomic orbitals. In particular, in the case of C_{60} fullerene, of sp^{2+x} orbitals. Such parametrization allows for an economic determination of the deformation potential associated with the different normal modes. The resulting electron-phonon coupling constants are used to calculate Jahn-Teller effects in C_{60}^- and multiple satellite peaks in the corresponding photoemission spectrum. The resulting cross section agrees well with the experimental data, better than any of the cross sections obtained making use of the electron-phonon coupling constants available in the literature [3,4,6–8]. Furthermore, the extension of the hybrid orbital model to describe the electron-phonon coupling phenomenon in fullerenes other than C_{60} as well as in nanotubes is simple to carry out.

The electron-phonon coupling is determined by the matrix element of the deformation potential

$$V_{\text{def}}(\vec{r}) = \sum_{\beta} \sum_{k=1}^3 (Q_{\beta})_k (\nabla_{\beta})_k V_e(\vec{r}, \{R\}) \Big|_{\{R\}=\{R^0\}}, \quad (1)$$

where $\{R\}$ represents the set of ionic coordinates with equilibrium values $\{R^0\}$, $(Q_{\beta})_k$ the

displacement field associated with the normal modes of the β -ion in the $k=(x,y,z)$ directions, while V_e is the total potential acting on the electrons. This potential can be expressed, in the local density approximation (LDA), as

$$V_e(\vec{r}, \{R\}) = V_{\text{pseudo}}^L(\vec{r}, \{R\}) + V_{\text{Hartree}}(\rho(\vec{r}, \{R\})) + V_{\text{xc}}(\rho(\vec{r}, \{R\})) + V_{\text{pseudo}}^{NL}(\vec{r}, \{R\}). \quad (2)$$

The first three terms are local and arise from: a) the pseudopotential associated with the ions; b) the Coulomb interaction acting among the electrons (Hartree field); c) exchange (Fock field) and correlation effects. The last term in Eq. (2) reflects the non-local part of the ionic pseudopotential.

Because the first and the last terms of Eq. (2) display simply an explicit dependence on the ion positions, the calculation of their gradient (cf. Eq. (1)) presents no difficulties. This is not the case for the second and third terms of Eq. (2), which depend on $\{R\}$ implicitly via the electronic density, a fact which can be used to write

$$\sum_{\beta} \vec{Q}_{\beta} \cdot \vec{\nabla}_{\beta} V_i[\rho(\vec{r}, \{R\})] = \sum_{\beta} \frac{\partial V_i[\rho]}{\partial \rho} \vec{Q}_{\beta} \cdot \vec{\nabla}_{\beta} \rho(\vec{r}, \{R\}), \quad (3)$$

where $i=(\text{Hartree}, \text{xc})$. Because in the LDA there is an explicit relation between V_i and ρ , the derivative $\partial V_i / \partial \rho$ can be calculated analytically. Consequently, the basic difficulty associated with the calculation of the deformation potential defined in Eq. (1), and thus of the electron-phonon coupling constants, lies in the calculation of the gradient of the electronic density along the normal displacements. To overcome this difficulty, we shall parametrize the LDA results in term of sp^{2+x} hybrid orbitals, in such a way that three of the four orbitals are directed along the carbon bonds of fullerene C_{60} , while the fourth takes care of the π -bonding present in the hexagons and is directed essentially perpendicularly to the fullerene surface.

In keeping with the fact that in C_{60} each atom has three nearest neighbours, the hybrid orbitals we are interested in can be written as

$$|\phi_1\rangle = a_1|s\rangle + b_1|p_x\rangle + c_1|p_y\rangle + d_1|p_z\rangle,$$

$$\begin{aligned}
|\phi_2\rangle &= a_2|s\rangle + \delta_2(m_2|p_x\rangle + n_2|p_y\rangle + t_2|p_z\rangle), \\
|\phi_3\rangle &= a_3|s\rangle + \delta_3(m_3|p_x\rangle + n_3|p_y\rangle + t_3|p_z\rangle), \\
|\phi_4\rangle &= a_4|s\rangle + \delta_4(m_4|p_x\rangle + n_4|p_y\rangle + t_4|p_z\rangle).
\end{aligned}
\tag{4}$$

Here $m_j = \cos \alpha_j$, $n_j = \cos \beta_j$, $t_j = \cos \gamma_j$, and α_j , β_j , γ_j ($j=2,3,4$) are the angles which define the direction of the bond between a Carbon atom and each of its three nearest neighbours, in a system of reference centered on the atom. After having fixed the direction of these orbitals, there still remain ten free parameters in Eq. (4), parameters which are completely determined by the orthonormalization condition.

To describe the radial dependence of the $|s\rangle$ and $|p\rangle$ orbitals, we have used the functions $R_s = \frac{2}{\sqrt{\sigma_1^3}}e^{(-r/\sigma_1)}$ and $R_p = \frac{2}{\sqrt{3\sigma_2^5}}re^{(-r/\sigma_2)}$, usually employed in the description of the Carbon atom. We have however adjusted the parameters σ_1 and σ_2 in order to obtain the best fit to the LDA C₆₀-density (see, for instance, Ref. [9]). One can then write the contribution to the total density arising from a single atom and, with the help of standard techniques, carry out a multipole expansion of this contribution around the center of the molecule. Adding the contributions of the 240 electrons one obtains the total density.

In Fig. 1 we display the two lowest multipoles of the C₆₀ ground state density, calculated in the LDA including exchange–correlation effects according to the parametrization of Perdew and Zunger [10]. The role of the Carbon atoms were taken into account in terms of norm–conserving pseudopotentials [11]. In the same figure we show the results of the hybrid orbital model, for $\sigma_1 = 0.78 \text{ \AA}$ and $\sigma_2 = 0.31 \text{ \AA}$ [12].

The next step consists in the calculation of the gradient of the density and, through Eqs. (3) and (4), the deformation potential. Within the hybrid orbital model, moving around the ions change the direction of the orbitals but not their shape. This means that the weights δ_j in Eq. (4) are fixed, and the only quantities which change are the angles α_j , β_j and γ_j . The calculation of $\vec{\nabla}\rho(\vec{r}, \{R\})$ becomes then quite simple.

In Fig. 2 we display the two lowest, and most important, multipole contributions of the local part of the deformation potential of C₆₀ for the lowest A_g phonon, corresponding

essentially to a breathing mode of the system, as calculated in the LDA. The wavenumber of this mode is equal to 491 cm^{-1} and to 496 cm^{-1} for C_{60} in solution and in the solid phase, respectively [13,14]. The wavenumber and zero point motion of the isolated molecule, calculated in the bond-charge model, are 493 cm^{-1} and $53.4\text{ }10^{-3}\text{ \AA}$, respectively [15]. As seen from Fig. 2, the hybrid orbital model provides an overall account of the ab-initio results. The discrepancies observed for small values of r for the multipole $(L,M)=(0,0)$ have little influence on the corresponding matrix elements, because the electronic wavefunctions are quite small around the origin of the molecule.

Making use of these results, one can calculate the electron-phonon coupling matrix elements in C_{60} . These are the matrix elements needed, for example, in the evaluation of the lineshape of allowed as well as of forbidden electronic transitions in C_{60} . To carry out similar calculations in C_{60}^- one should employ a deformation potential which is evaluated by making use of the electronic density of the negative ion, at the ground state geometry. Because the density of the 240 valence electrons of C_{60} is not appreciably altered by adding one more electron, one expects the deformation potentials associated with C_{60} and C_{60}^- to be quite similar. In fact, we have carried out fully relaxed, ab-initio calculations of the matrix elements in C_{60}^- and found that they agree with those of C_{60} within less than 10%. In keeping with these results, the electron-phonon matrix elements calculated starting from the C_{60} electronic density and ground state ionic configuration are used in the following.

In C_{60}^- the state t_{1u} is occupied with a single electron. This level is separated by an energy of the order of the eV from neighbouring levels, while the electron-phonon coupling matrix elements to be found below are of the order of the meV. Consequently, it seems justified to consider, within the present context, that the electronic motion is confined to the t_{1u} level. Under such circumstances, and because of symmetry reasons, the only possible couplings are to phonons with A_g and H_g symmetries (cf., e.g., Ref. [7]).

The matrix elements $\langle t_{1u}\nu | V_{\text{def}} | t_{1u} \rangle$, where ν stands for the quantum numbers of the phonon, are related to the partial electron-phonon coupling constant $\lambda_\nu/N(0) = \alpha g_\nu^2/\omega_\nu$, according to $\langle t_{1u}\nu | V_{\text{def}} | t_{1u} \rangle = (g_\nu/2) W_{nm}^l$ (cf., e.g., Ref. [16] and Refs. therein). In the

above expression $N(0)$ is the density of levels at the Fermi energy, α is equal to $1/3$ for A_g phonons and $5/3$ for H_g phonons, while ω_ν is the energy of the phonon. The quantities W_{nm}^l are geometric coefficients, the index l distinguishing between the different degenerate states of each phonon (H_g is five-fold degenerate while A_g is single-fold degenerate).

In Table I we display the multipole contributions to the matrix element $\langle t_{1u} A_g | V_{\text{def}} | t_{1u} \rangle$, associated with the lowest energy A_g mode calculated making use of the LDA and of the hybrid orbital model. The different contributions of the model display the same sign and similar order of magnitude as those calculated in LDA, while the summed contribution agree within 20%.

Following the same steps as those leading to the results displayed in table I, the different matrix elements $\langle t_{1u} \nu | V_{\text{def}} | t_{1u} \rangle$ ($\nu=A_g, H_g$) have been calculated. Our results have been compared with those from other theoretical calculation available in the literature [3,4,7,8], as well as with the empirical values obtained from Gunnarsson's systematic analysis of the photoemission spectra of C_{60}^- [6]. While this analysis indicates that the coupling of the t_{1u} electron to the $H_g(2)$ leads to the largest value of $\lambda_\nu/N(0)$, the results reported in Refs. [3,4,7,8] indicate the coupling to the $H_g(7)$ -phonon to be the most important. In the hybrid orbital model discussed above, the largest coupling of the t_{1u} level is to the $H_g(2)$ -phonon, in agreement with the analysis by Gunnarsson and co-workers [17].

Making use of the matrix elements $\langle t_{1u} \nu | V_{\text{def}} | t_{1u} \rangle$ ($\nu=A_g, H_g$) calculated in the hybrid orbital model, and of the results of the bond charge model [15] to describe the properties of the phonons, we have solved the total electron-phonon Hamiltonian containing an electronic term, a phonon term, and a linear coupling term (cf., e.g., Ref. [6]) in a basis of one t_{1u} electron and up to three phonon states. The lowest eigenvalue $|\widetilde{t_{1u}}\rangle = C^{(0)} |t_{1u}\rangle + \sum_\nu C_\nu^{(1)} |t_{1u} \otimes \nu\rangle + \dots$ was calculated using the Lanczos method. The first term in $|\widetilde{t_{1u}}\rangle$ describes a state with no phonons, the second term a state with one phonon, etc. Making use of these results, we have calculated the photoemission cross section assuming the sudden approximation, where the emitted electron does not interact with the system left behind [6].

In Fig. 3 we show the results of the hybrid orbital model, in comparison with the results of the analysis of the photoemission data carried out by Gunnarsson and co-workers [6]. Although the hybrid orbital model leads to a somewhat weaker electron–phonon coupling than required by the experimental finding, and consequently to a somewhat too large value of $C^{(0)}$, it provides a much better account of the empirical spectrum than the other theoretical models, whose partial electron–phonon coupling constant have been reported in Refs. [3,4,7,8] (cf. also table I of Ref. [6]).

We conclude that the hybrid orbital model of the electron–phonon coupling displays a number of attractive features: i) it leads to matrix elements of the deformation potential which reproduce quite accurately the results of ab-initio calculations; ii) it provides an excellent account of the photoemission spectra of C_{60}^- ; iii) it is quite economic to use, and can be extended at profit to fullerenes other than C_{60} as well as to nanotubes.

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TABLES

TABLE I. Different multipole contributions to the matrix element $\langle t_{1u} A_g | V_{\text{def}} | t_{1u} \rangle$, associated with the lowest energy A_g mode of C_{60} (t_{1u} is the LUMO of the molecule).

L=	Matrix Element [meV]	
	LDA	Hybrid Orbital Model
0	-47.739	-49.506
6	-3.319	-2.369
10	19.741	20.275
12	-1.030	-2.828
16	6.082	5.869
18	14.940	15.473
20	2.139	1.777
Total	-9.399	-11.309

FIGURES

FIG. 1. Comparison between the results of LDA (full lines) and Hybrid Orbital Model (dashed lines) for the two main multipole contributions to the ground state density of C_{60} . (a) and (b) refer to the $(L,M)=(0,0)$ and $(6,0)$ contributions respectively.

FIG. 2. Same as Fig. 1 for the two main multipole contributions to the deformation potential associated with the lowest A_g phonon of C_{60} .

FIG. 3. Results for the photoemission spectrum of C_{60}^- , obtained making use of the electron-phonon matrix elements calculated in the present paper as well as in previous theoretical works [3,4,7,8]. The solid curve correspond to the experimental results [6].







